DIHYDROAMORPHIGENIN FROM THE SEEDS

OF Amorpha fruticosa

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We have previously [1] reported that chromatograms of extracts of the fruit of various species of Amorpha show the presence in them of three groups of rotenoids with different polarities.

On repeated chromatography on columns of silica gel and alumina in the benzene-methanol (9:1) system, from the group of rotenoids with the lowest polarities we have isolated – in addition to amorphigenin, 7,8-dehydroamorphigenin and amorphigenol – a small amount (0.005%) by weight of the fruit) of a new substance, $C_{23}H_{24}O_7$, mp 189-190°C. In the Durham [2] and Goodhue [3] reactions for rotenoids this substance gives a positive reaction, and with the Keller-Kiliani reagent it forms a cherry-red coloration [4]. Its UV and IR spectra are extremely close to the corresponding spectra of amorphigenin and show its rotenoid structure.

The mass spectrum of the substance also confirms its rotenoid nature [5, 6]. The molecular ion has 412 units (two units greater than that of amorphigenin). The presence in the spectrum of the maximum peak of the ion with m/e 192 and the products of its further fragmentation with m/e 191, 177, 161, 149, and 147 show that the structure of the benzopyran part of the molecule of the rotenoid under study is analogous to that of the corresponding part of the amorphigenin molecule.

The mass spectrum has peaks of ions of types a and b formed from different parts of the molecule [6]. The presence of ion a $(m/e\ 219)$ shows the common nature of the structures of the benzopyran part of the rotenoid and of amorphigenin. Ion b has $m/e\ 221$, i.e., two units greater than that for amorphigenin. Consequently, the structures of amorphigenin and of the rotenoid under investigation differ in the benzo-furan part of the molecule.

It is obvious that the difference of two units can be explained only by the addition of one molecule of hydrogen. If the structure of the benzofuran moiety of amorphigenin is considered, it becomes clear that this addition can take place only at the double bond in the side chain.

In actual fact, the mass spectrum of the new rotenoid shows, in addition to the fragments mentioned, the peak of an ion with m/e 353 (M-59) with an intensity of about 10% of the maximum peak, the formation of which can be explained by the splitting of a hydroxyisopropyl side chain. In amorphigenin and rotenone, because of the presence of the $C_{22} = C_{23}$ double bond the analogous peak is either extremely small or completely absent [5, 6]. At the same time, in the mass spectrum of amorphigenol in which this double bond is hydrated, the corresponding peak likewise has a fairly high intensity (10% of the maximum peak) [1].

On the basis of the facts given, we propose for the rotenoid concerned the structure of 22,23-dihydroamorphigenin (22,23-dihydro-24-hydroxyrotenone).



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